

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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|--------------------|---|------------------|-------------------|
| Applicants: | Youhao Xu, et al. | Examiner: | Jennifer A. Leung |
| Serial No.: | 09/553,990 | Art Unit: | 1764 |
| Filed: | April 20, 2000 | Docket: | 23242 |
| For: | RISER REACTOR FOR FLUIDIZED CATALYTIC CONVERSION | | |

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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. §1.132

Sir:

I, Xieqing Wang, hereby declare as follows:

1. I am a Chinese Citizen residing in Beijing, People's Republic of China.
2. I am an Academician of the Chinese Academy of Engineering and the chairman of the Academic Degree Evaluation Committee at Research Institute of Petroleum Processing (RIPP), SINOPEC. I've been working at RIPP for 47 years.
3. From September 1951 to July 1956, I studied in the Department of Petroleum Refining at China University of Petroleum-Beijing and obtained my Bachelor's degree; from September 1956 to July 1961, I studied in Technische Hochschule für Chemie, Germany, and obtained my PhD.
4. I have devoted my career to the development of catalytic cracking technology in RIPP, and have more than 40 years experience in this technology. Presently, I am in charge of developing Deep Catalytic Cracking (DCC) technology and Maximizing Gas and Gasoline (MGG) technology as well as many new catalysts development in the field of fluidized catalytic cracking (FCC). I have published more than 80 papers and have obtained 40 granted patents bearing my name in the field of catalytic cracking.

5. I have been an author of a number of scientific publications, especially in the field of FCC, which is closely related to the subject application. A list of my publications is attached hereto as **Exhibit A**.

6. I have reviewed the specification of U.S. Patent Application Serial No. 09/553,990 ("the '990 application") and am familiar with the contents therein. The '990 application presently claims a fluidized catalytic cracking (FCC) riser reactor having two reaction zones. One of the features of the riser reactor of the '990 application is that the ratio of the diameter of the second (upper) reaction zone relative to the diameter of the first (lower) reaction zone is in the range from about 1.5:1 to about 5:1.

7. One of the main objectives of the '990 application is for producing clean gasoline with a low olefin content and enhanced liquid yield. The technology described in the '990 application is also referred to as "Maximizing Iso-Paraffins" or "MIP" for short, and the FCC riser reactor disclosed and claimed in the '990 application is also referred to as an MIP reactor or apparatus. The MIP reactor of the '990 application achieves a significant reduction of the olefin content in gasoline from a level of 40%-60% by weight to a level of 10%-30% by weight. Simultaneous with this olefin reduction, the MIP reactor also achieves production of desirable products such as iso-paraffin. I have been asked to comment on whether these results achieved using the claimed FCC riser reactor would have been unexpected to those skilled in the art.

8. It is my scientific opinion that the results achieved by the claimed MIP riser reactor of the '990 application were entirely unexpected to those skilled in the art. My opinion is based on my evaluation and familiarity of the art relating to the FCC technology.

9. The MIP reactor of the '990 application is a new type of FCC reactor that has achieved significant reduction of olefin in gasoline and simultaneous improved product profile, without causing over-cracking. The MIP reactor of the '990 application is designed to have two reaction zones, a first (lower) reaction zone and a second (upper) reaction zone. Characteristic features of the MIP reactor include, among other things, a ratio of diameter (i.e., the diameter of the second reaction zone relative to the diameter of the first reaction zone) that is in the range from about 1.5:1 to about 5:1. This structural design allows for a short residence time in the first reaction zone and a longer residence time, i.e., longer than 3 seconds, or even 5 seconds or greater, in the second reaction zone. Given this design, heavy hydrocarbon feedstock is cracked in the first reaction zone at a high temperature and a short residence time into a lighter

hydrocarbon feedstock and olefin; then, in the second reaction zone where the diameter is larger than that of the first reaction zone, the olefin produced in the first reaction zone is effectively converted to iso-paraffin at a lower temperature during a longer residence time through hydrogen transfer reactions, etc.

10. In China, about 80% of commercial gasoline is produced by using the FCC technology, and the gasoline produced by such technology has a high content of olefin, for example, 40-60% by weight, as compared to less than 30% by weight seen in most other countries. It is becoming increasingly necessary to reduce the content of olefin from gasoline produced by FCC technology in order to meet current environmental regulations. Significantly, the MIP reactor of the '990 application achieves a significant reduction of the olefin content in gasoline from a level of 40%-60% by weight to a level of 10%-30% by weight.

11. Prior to the filing of the '990 application, no single riser reactor in the FCC field was available that could effectively reduce the content of olefin in gasoline and simultaneously produce more desirable products such as, for example, iso-paraffin.

12. For example, the FCC riser reactor disclosed in EP 0,171,460 (hereinafter EP '460), which the Examiner has applied as prior art in the '990 application, was primarily designed to use dry gas (containing little C_{3+} and almost no C_{5+}) as the lift gas at the bottom of a FCC riser so as to achieve lower coke production and better product selectivity. There is simply no disclosure in EP '460 with respect to employing the riser reactor for olefin reduction. Further, the riser reactor disclosed in EP '460 would not, in my opinion, achieve effective reduction of olefin and simultaneous production of desirable products in any event. In the first instance, the riser reactor of EP '460 is designed to have an expanded (e.g., larger diameter) portion which provides a high temperature and a short contact time (i.e., residence time). See page 40, lines 15-21. EP '460 teaches that the contact time should be no more than 3 seconds (see page 41, lines 7-10), and the short contact time can reduce the tendency of over-cracking to occur. See page 49, lines 20-24. In contrast to the MIP reactor of the '990 application, the riser reactor of EP '460 allowing for only a short contact time would not have been effective to reduce olefin, especially high levels (40-60% wt) of olefin. If one were to alter the structural design of the reactor of EP '460 in order to have a longer contact time, this would have led to over-cracking according to EP '460 (page 49, lines 20-24), thereby resulting in a decrease in the production of valuable products. The MIP riser reactor of the '990 application typically has an outlet section in which

the diameter is sharply narrowed compared with the diameter of the second reaction zone in order to obtain sufficient momentum for separating the catalysts from the gas-solid mixture. In contrast, the riser reactor disclosed in EP '460 does not have an outlet section, and there is no need to have such a section in the reactor of EP '460 because a very limited expansion within the upper section provides sufficient momentum for such separation.

13. Another FCC riser reactor, documented in the art after the filing of the '990 application, is a two-stage riser for fluidized catalytic cracking (also known as TSRFCC). See, e.g., Hong-Hong Shan, et al., "Maximum FCC diesel yield with TSRFCC technology", *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 2003, 48(2), page 710-711 (copy attached as **Exhibit B**). A TSRFCC reactor is designed to reduce olefins in gasoline. A TSRFCC reactor uses two risers to reduce the olefin content in gasoline by recycling the gasoline component from the first riser into the second riser. See Figure 1(b) of the Shan et al. reference. Compared with the present application (e.g., an MIP riser reactor), the TSRFCC reactor has considerable operational, cost and efficiency disadvantages associated therewith. Moreover, since two risers are required in a TSRFCC reactor, the operation of the TSRFCC reactor is more difficult than the MIP reactor of the '990 application, and the energy consumed is much more than the energy consumed by the inventive MIP reactor. In a TSRFCC reactor, the gasoline product from the first riser is recycled into the second riser for the purpose of reducing olefin content in gasoline. As such, some of the gasoline products are certainly lost due to further cracking reactions and production of by-products such as dry gas, slurry and coke that take place in the TSRFCC reactor. In other words, the MIP reactor provides more valuable products than a TSRFCC reactor. From an operational view point, as well as an economic and environment view point, the MIP reactor disclosed and claimed in the instant application is superior as compared with the TSRFCC technology disclosed above.

14. The claimed MIP reactor of the '990 application, by combining the two concepts of "higher temperature and shorter residence time" and "lower temperature and longer residence time" in one single riser reactor with an enlarged section in the middle part of the riser, has achieved a synergism for olefin reduction and iso-paraffin production, with relatively minimum operation difficulty, investment cost and energy consumption. It is my opinion that these results achieved by the riser reactor of the '990 application are unexpected and represent tremendous improvements over the prior art.

15. Further, it is my opinion that the extent of reduction of olefin achieved by the riser reactor of the '990 application is also unexpected.

16. As disclosed in the '990 application, the riser reactor reduced the content of olefin to a level below 30% by weight (15.17wt%, 20.51 wt %, and 28.11 wt %, as exemplified in Examples 3, 2 1, and Table 7, 6, 4, respectively in the specification), and simultaneously produced iso-paraffin in an amount of about 36% by weight or greater (36.0 wt %, 41.83 wt %, and 43.86 wt %, respectively). In contrast, the amounts of olefin and iso-paraffin in the gasoline from a conventional FCC riser reaction are 56.49% by weight and 11.83% by weight, respectively. See Examples 1-3 and Comparative Example 1 of the '990 application. The degree of improvement over a conventional FCC riser reactor is dramatic and unprecedented in the FCC field.

17. I have also reviewed the Declaration of Dr. Youhao Xu submitted to the Patent Office on April 4, 2008 ("the Declaration"). In the Declaration (see page 9, Table 4), the criticality of the ratio of diameters of the second reaction zone versus the first reaction zone was evaluated by comparing a riser reactor having a diameter ratio of 1.2:1 (outside of the claimed range), with riser reactors having ratios within the claimed range, as disclosed in the '990 application. The reactor with a ratio of 1.2:1 only reduced olefin to 40.69% by weight (as opposed to 20.51-28.56% by weight by the claimed reactor), and produced iso-paraffin at 21.33% by weight (as compared to 34.8 - 43.86% by weight by the claimed reactor). The significance of the diameter ratio is apparent and substantial from these data.

18. I have also reviewed U.S. Patent No. 5,167,795 to Gartside ("Gartside"). It is my opinion that reliance on Gartside is inappropriate in assessing the results or the degree of improvement achieved by the FCC riser reactor of the '990 application. First, Gartside teaches a top-down flow tubular reactor (see column 4, lines 38-47), which is completely different from an up-flow FCC riser reactor as presently claimed. Second, the teaching of Gartside is limited to the transition from pyrolysis to cracking, rather than the transition within the cracking process, as is the case of the '990 application. Specifically, as evidenced by Table I of Gartside, when the residence time and reactor temperature of pyrolysis is, respectively, increased from 0.3 seconds to 2.0 seconds, and reduced from 816°C to 565°C, a transition from pyrolysis to cracking occurs,

and the ratio of paraffin to olefin is improved from 0.05 (the pyrolysis step) to 0.73 (the cracking step). This shows that longer residence times and lower temperatures favor paraffin production over olefin only in the context of changing from pyrolysis to cracking. Gartside further teaches that when the residence time within a cracking process is reduced from 2 seconds to 0.9 seconds, and the temperature is reduced from 565°C to 510°C, the ratio of paraffin to olefin is improved from 0.73 to 1.14. This result, at most, appears to suggest that shorter residence times and lower temperatures may favor paraffin production over olefin, but this is clearly different from longer residence times and lower temperatures, as disclosed in the '990 application. Furthermore, when the residence time is reduced from 2 seconds to 0.15 seconds, and the temperature is reduced from 565°C to 540°C, the ratio of paraffin to olefin is reduced from 0.73 to 0.46. This result appears to suggest that shorter residence time and lower temperature may disfavor paraffin production over olefin, which is also different from what is disclosed in the '990 application. Therefore, considering the different effects of residence time and temperature on the production of paraffin over olefin in the cracking process, which were observed in a top-down flow tubular reactor, it is my opinion that the teaching of Gartside is irrelevant to assessing the results or the degree of improvement achieved by the FCC riser reactor of the '990 application.

19. The substantial and effective reduction of olefin in gasoline and simultaneous production increase of iso-paraffin in gasoline, achieved by one simple riser reactor of the '990 application, is entirely unexpected to me and others in the FCC field. The technological, economical and environmental advantages brought by the '990 application are simply unprecedented.

20. I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and that further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of the Application or any patent issuing therefrom.

Dated this 6 day of Nov. 2008.
Xieqin Wang
Signature

EXHIBIT A

The list of the publications of Mr. Xieqing Wang

Granted US Patents invented by Mr. Xieqing Wang

1. 7,375,256 Catalytic conversion process for producing light olefins with a high yield petroleum hydrocarbons
2. 6,939,823 Stripper and a stripping process for removing the flue gas carried by regenerated catalyst
3. 6,723,292 Stripper and a stripping process for removing the flue gas carried by regenerated catalyst
4. 6,495,028 Catalytic conversion process for producing isobutane and isoparaffin-enriched gasoline
5. 6,475,465 Titanium-silicalite molecular sieve and the method for its preparation
6. 6,342,153 Pillared clay catalysts for heavy oil catalytic pyrolysis process and the preparation method thereof
7. 6,210,562 Process for production of ethylene and propylene by catalytic pyrolysis of heavy hydrocarbons
8. 6,080,698 Pentasil-type molecular sieve containing composition and its preparation method

Papers published by Mr. Xieqing Wang

1. Commercial trial of catalytic pyrolysis process for manufacturing ethylene and propylene.

Xie, Chaogang; **Wang, Xieqing**; Guo, Zhixiong; Wei, Qiang

(Research Institute of Petroleum Processing, SINOPEC, Peop. Rep. China).

Proceedings of the World Petroleum Congress, 17th(Vol. 3), 547-554 (English) 2002
Institute of Petroleum. CODEN: WPCPAU. ISSN: 0084-2176. DOCUMENT
TYPE: Journal CA Section: 51 (Fossil Fuels, Derivatives, and Related Products)

Research Institute of Petroleum Processing, SINOPEC, developed a novel ethylene and propylene production technology, Catalytic Pyrolysis Process (CPP), based on the modification of DCC process via operating parameter, catalyst formulation, and unit configuration. A riser reactor and a specially designed zeolite catalyst were used in this technology. At 883 K, 13.71 m % ethylene and 21.45 m % propylene were obtained. At 913 K, the ethylene and propylene yields were 20.37 and 18.23 m %, respectively, with 45% Daqing VGO and 55% vacuum residue mixture feedstock. The ethylene yield of CPP process was lower than that of steam cracking, but the yield of propylene and butylenes in CPP process were higher than that of steam cracking. Total gaseous olefins yields were the same in both processes. Benzene content in CPP in naphtha fraction was lower than that of steam cracking and toluene and xylenes contents were more than that of steam cracking. 4 graphs, 4 tables

2. Catalytic processes for light olefin production.

Wang, Xieqing; Xie, Chaogang; Li, Zaiting; Zhu, Genquan

(Research Institute of Petroleum Processing, SINOPEC, Beijing, Peop. Rep. China).
Practical Advances in Petroleum Processing, Volume 1, 149-168. Edited by: Hsu, Chang S.; Robinson, Paul R. Springer: New York, N. Y. ISBN: 0-387-25811-6(English) 2006.

3. Catalytic pyrolysis process (CPP) - An upswing of RFCC for ethylene and propylene production.

Wang, Xieqing; Shi, Wenyuan; Xie, Chaogang; Li, Zaiting

(Research Institute of Petroleum Processing, SINOPEC, Beijing, Peop. Rep. China).
Pre-Print Archive - American Institute of Chemical Engineers, [Spring National Meeting], New Orleans, LA, United States, Mar. 11-14, 2002, 983-990. American Institute of Chemical Engineers: New York, N. Y. (English) 2002.

4. Residue catalytic cracking to produce light olefins and gasoline

Chen, Z.B.; Huo, Y.Q.; Zhong, L.S.; Wang, Z.Y.; **Wang, X.Q.**

(Research Inst of Petroleum Processing)

American Chemical Society, Division of Petroleum Chemistry, Preprints, v 40, n 4, Aug, 1995, Petroleum Chemistry and Processing, p 773-775

5. Deep catalytic cracking process for light-olefins production.

Li, Zaiting; Shi, Wenyuan; **Wang, Xieqing;** Jiang, Fuking

(Research Institute of Petroleum Processing, China Petrochemical Corporation (SINOPEC), Beijing 100083, Peop. Rep. China).

ACS Symp. Ser., 571(Fluid Catalytic Cracking III), 33-42 (English) 1994.

6. Catalyst hydrothermal deactivation and coke formation in catalytic pyrolysis process for ethylene production

Xie, Chaogang; Zhang, Zhigang; Li, Zaiting; **Wang, Xieqing**

(Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, Peop. Rep. China).

Am. Chem. Soc., Div. Pet. Chem., 45(2), 317-319 (English) 2000 American Chemical Society, Division of Petroleum Chemistry.

7. ^{27}Al , ^{29}Si , and ^{31}P NMR study of ZRP series zeolite. A modified HZSM5 type zeolite series.

Wang, Xieqing; Yue, Shufan; Fu, Wei (Research Institute of Petroleum Processing, Beijing 100083, Peop. Rep. China).

Shiyou Lianzhi Yu Huagong, 28(Suppl.), 10-16 (English) 1997

8. Pillared rectorite microspheric catalyst for cracking heavy oil.

Guan, Jingjie; Yu, Zhiqing; Chen, Zhenyu; Liu, Qinglin; **Wang, Xieqing**

(Research Institute of Petroleum Processing, China Petro-Chemical Corporation,
Beijing 100083, Peop. Rep. China).
Am. Chem. Soc., Div. Pet. Chem., 42(2), 489-492 (English) 1997 American Chemical
Society, Division of Petroleum Chemistry

EXHIBIT B

Maximum FCC diesel yield with TSRFCC technology

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Introduction

After a quite long time exploration, steadily heavier crude oil is becoming one of the toughest frontiers in fluid catalytic cracking (FCC) process. Almost at the same time, stringent environmental constraints also put a big pressure on FCC process to readjust its product distribution and improve its product quality.

In recent years, many upgrades and modification have been done for RFCC units. In terms of process technology, MSCC^[1], Down-Flow FCC^[2], Double-Riser FCC^[3] and Two-Stage Riser FCC^[4,5] (TSRFCC) were developed one by one. Another term is advanced by FCC equipment enhancement such as novel feed nozzle^[6], fast separating system at riser outlet^[7], high-efficiency regenerator, multi-step reactor strippers, and riser terminations, etc. Among these technologies and studies, obviously, most are merely peripheral modification around the FCC riser reactor; quite few touched the very course of FCC reaction except that MSCC and Down-Flow FCC are on the way to real industrialization.

Riser reactor, commonly applied by worldwide FCC (One-Stage Riser, OSRFCC) process, was proved that, in the second half of riser, the activity and selectivity of the catalyst drop dramatically and over-cracking of intermediate products occurs^[8], which deteriorate markedly the product distribution and final products properties. Based on this fact, a novel FCC process named TSRFCC had been invented successfully in china. The features of this new process are attributed to catalyst in relay, subsection reaction, high catalyst/oil (C/O) ratio and short residence time, through which the average activity and selectivity of the catalyst are enhanced and undesirable secondary reaction and thermal reaction are suppressed efficiently. Some former studies proved that TSRFCC process open a fairly good way to maximize gasoline yield. But under the atmosphere of insufficient supply of diesel in the worldwide market, especially in China, how to maximize diesel/gasoline ratio is a very important and urgent task. TSRFCC-I technology, a modified TSRFCC process had been studied on this paper to fulfill the task.

The Configuration and Theory of TSRFCC-I

The primary difference between TSRFCC and TSRFCC-I is that in the latter process the diesel cut produced by the first stage riser is removed from the internal products, then the rest parts of gasoline and heavy oil being injected into the second stage riser instead of overall internal products in series in the original TSRFCC process. Figure 1 shows the principle flow chart of both OSRFCC and TSRFCC processes. In the modification of commercial plants, the internal fractionating tower will be a new one or the former one.

Firstly, TSRFCC-I inherits the original features of catalyst in relay and subsection reaction to ensure oil vapor contact regenerated catalyst in both stages. Secondly, removing internal diesel produced by the first stage avoids its over-cracking in the second stage, thus maximum diesel yield can be achieved. Thirdly, removing internal diesel enhances the heavy oil conversion to light oil in the second stage, illustrated by chemical balance of catalytic cracking reaction.

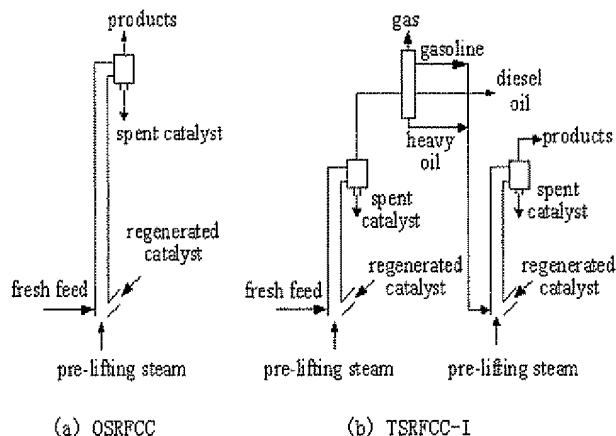


Figure 1 Comparison between OSRFCC and TSRFCC-I

Experimental

The performance of TSRFCC-I was evaluated in a pilot FCC plant^[4]. One mixture of 65wt%VR + 35wt%VGO was employed as feedstock, the properties in Table 1. Catalyst used is commercial equilibrium catalyst ZC-7300, the microactivity is 60. Gaseous products were analyzed in HP5890II and Varian GC-3800C, and liquefied products in HP5880A.

Table 1 Property and composition of FCC feedstock

| Density(20°C, g/ml) | | 0.9205 | CCR (wt%) | | 4.62 |
|--------------------------|------------|--------|------------------------|-----|-------|
| Group components (wt%) | saturated | 52.37 | Metal Content (ppm) | Fe | 2.52 |
| | aromatics | 30.08 | | Ni | 4.90 |
| | resin | 17.47 | | Cu | / |
| | asphaltene | 0.076 | | V | 0.095 |
| element components (wt%) | H | 12.67 | Distillation range(°C) | 0% | 331 |
| | C | 85.91 | | 10% | 467 |
| | N | 0.31 | | 20% | 491 |
| | S | 0.16 | | 30% | 518 |

The main reaction conditions include temperature 490–520°C, the ratio of catalyst to feedstock 6, and residence time 1.5–2.2 s.

Results and Discussion

Yield Distribution Table 2 shows the product distributions of two different technologies. Compared with OSRFCC, at high conversion, TSRFCC-I showed a 6-7 percent point increase in diesel yield, accompanied by a 1.5-2 percent point increase in light oil while maintaining the same level of liquid product yield. Moreover, a 2 percent point decrease of dry gas yield was achieved. Obviously, reduced effect of thermal cracking had been confirmed as well as the yield distribution of TSRFCC-I had been markedly improved.

Table 2 Product structure of OSRFCC and TSRFCC-I

| Pro. Distri. (wt%) | OSRFCC | | TSRFCC | |
|-----------------------|--------|-------|--------|-------|
| hydrogen | 0.19 | 0.14 | 0.11 | 0.15 |
| dry gas | 4.27 | 4.42 | 2.3 | 2.68 |
| LPG | 19.72 | 17.84 | 17.73 | 18.27 |
| gasoline | 50.07 | 50.47 | 45.11 | 44.86 |
| diesel | 15.15 | 14.13 | 23.44 | 21.87 |
| heavy oil | 4.41 | 5.84 | 3.24 | 3.75 |
| light oil | 65.23 | 64.6 | 68.56 | 66.73 |
| coke | 6.38 | 7.30 | 8.17 | 8.57 |
| liquid product yield* | 84.94 | 82.44 | 86.29 | 85 |
| Conversion** | 95.59 | 94.16 | 96.75 | 96.25 |

* Liquid product yield = LPG + gasoline + diesel

** Conversion = (100 – heavy oil)%

It is commonly believed that dry gas is produced by thermal cracking abiding by free radical mechanism. In the second half of conventional riser with 3 second above residence time, oil vapor can't fully contact acid sites due to deposited coke on the catalyst, so high temperature increases thermal cracking dramatically and quickly, as a result, increasing dry gas yield appears. In the course of TSRFCC-I, at the outlet of first stage riser oil vapor is separated with the deactivation catalyst in time before impending increasing thermal cracking, then injected into the second stage to contact with the regenerated catalyst exhibiting great accessibility of active sites. Consequently, thermal cracking was reduced radically and dry gas yield was minimized accordingly.

In the term of diesel, TSRFCC-I showed a 6-8 percent point increase compared with OSRFCC at similar conversion. It can be explained by two reasons. Firstly, removing internal diesel as final product prevent it from over-cracking in the second stage. Secondly, a great amount of active sites on the catalyst in the second stage cater for the heavy oil cracking well, which make speed of diesel producing surpass cracking. Diesel yield and diesel/gasoline ratio can therefore be maximized, which satisfies the changing trend of marketing structure.

Light oil yield in TSRFCC-I is 1-2 percent point higher than that in OSRFCC at highly extended conversion while keeping sound yield structure. Even though gasoline yield is relatively low in TSRFCC-I via cracking twice, the increase of diesel yield compensate the decrease of light oil for the loss of gasoline yield excessively.

As far as coke is concerned, the relatively high yield may be related to the hydrocarbons entrapped in the pores of the catalyst and carried through the inefficient stripping. This situation will be improved in FCC commercial unit.

To fully utilize TSRFCC-I technology, an optimum internal conversion must be controlled. Inappropriate internal conversion will definitely break the balance of two stages and deteriorate the course of reaction in whichever stage unavoidably, so the overall product structure is doomed to get worse. Numerous experiments proved that an optimum internal conversion must be chosen at the point where the high yield and selectivity of light oil in first stage was obtained and catalysis of catalyst dropped evidently. Only by doing so, two stages can run effectively and intimately.

Product Properties Data concerning the composition of LPG are shown in Table 3. The total yields of propylene and butylenes in TSRFCC-I are 85wt% above, versus 81wt% below in OSRFCC, higher 4 percent point. Higher light olefin yield in FCC unit is compatible with the trend of increasing demand of petrochemical feedstock.

Table 3 C₃ and C₄ olefins contents (wt%) in LPG

| Olefin | OSRFCC | | TSRFCC | |
|----------------|--------|-------|--------|-------|
| C ₃ | 33.56 | 34.56 | 40.15 | 37.70 |
| C ₄ | 47.27 | 40.83 | 47.23 | 47.49 |
| Total olefin | 80.84 | 75.39 | 87.38 | 85.20 |

Used feedstock, a kind of paraffin-rich oil, is potentially efficient to produce smaller olefins by catalytic cracking leading to higher olefin content in FCC gasoline. This explains why gasoline produced by paraffin-based crude is generally unqualified for the environmental regulations. At the same conversion, gasoline in TSRFCC-I, compared with OSRFCC, gives a similar content of n-paraffins, an increase of i-paraffins, a considerably deduction of olefins as well as an increase of octane number. The composition data of gasoline are present in Table 4.

Table 4 Gasoline composition of OSRFCC and TSRFCC-I (wt%)

| Items | OSR1 | TSR1 | OSR2 | TSR2 | OSR3 |
|------------------|-------|-------|-------|-------|-------|
| Conversion | 80 | 96.56 | 76.27 | 96.75 | 95.78 |
| n-paraffin | 5.58 | 5.40 | 5.36 | 5.42 | 5.11 |
| i-paraffin | 23.65 | 28.12 | 25.79 | 29.90 | 24.00 |
| naphthene | 7.79 | 8.07 | 8.00 | 7.65 | 6.34 |
| aromatic | 18.86 | 25.45 | 16.82 | 18.75 | 19.02 |
| olefin | 44.31 | 33.13 | 44.09 | 38.29 | 45.47 |
| RON | 90.9 | 94.2 | 90.9 | 93.2 | 93.2 |
| MON | 78.0 | 80.8 | 78 | 80.0 | 80.0 |
| Anti-knock index | 84.4 | 87.5 | 84.4 | 86.6 | 86.6 |

The feed is nearly converted completely in the present of catalyst via two stages. Employing regenerated catalyst and higher C/O ratio brought by subsection reaction in the second stage increase the amount of accessible active sites, which would lead to more hydrogen transfer, so more gasoline olefins would be saturated, otherwise, the probabilities of isomerization and aromatization also increased, as a result, the gasoline olefinicity went down significantly. Higher octane numbers of increased aromatics and i-paraffins than decreased olefins account for the little enhancement of gasoline octane numbers.

Conclusions

The novel TSRFCC-I process (vs. OSRFCC) has a great impact on yield structure, conversion and products properties. Removing diesel cut from internal products boosts overall conversion, maximizes the production of diesel and diesel/oil ratio, minimizes the content of olefins in gasoline, and improves the qualities of LPG and gasoline. Due to the unique configuration of TSRFCC-I process, maximizing the profitability of FCC units will become possible in the near future.

Acknowledgement. This work was Supported by the PetroChina.

References

- (1) Chang, T., Louisiana Refinery Revamp Takes Advantage of Heavy Sour Margins. *Oil & Gas J.*, 26(45), 68-72(1998).
- (2) Ren-sheng Deng, Teng-fei Liu, Fei Wei, Yong Jin, Composition of the Process in Riser and Downer Reactors, *Chemical Reaction Engineering and Technology*, 17(3), 238-243(2001).
- (3) Hai-tao Tang, Research and Development of Flexible Multi-Functional FCC process, *Petroleum Refinery Engineering*, 31(6), 8-10(2001).
- (4) Jian-fang Zhang, Hong-hong Shan, Zheng Li, Gen-lin Niu, Yu-dong Sun, New Development of FCC Through Two-staged Riser in Series. I. The Reactor of Two-staged Riser, *ACTA PETROLEI SINICA(PETROLEUM PROCESS SECTION)*, 16(5), 66-69(2000).
- (5) Zheng Li, Jianfang Zhang, Honghong Shan, Zhongxiang Han, Feng Du, Development of Two-stage Riser FCC Technology II. Increase of The Light Fraction Yield and Decrease of The Olefins Content in Gasoline, *ACTA PETROLEI SINICA(PETROLEUM PROCESS SECTION)*, 17(5), 26-29(2001).
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